Supporting information:

C_{60}/TiO_x Bilayer for Conformal Growth of Perovskite Film for UV Stable Perovskite Solar Cells

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Experimental Section

1. Materials: C_{60} (99.5%) and $TiCl_4$ (98%) were respectively purchased form Alfa Aesar (U.S.) and Sinopharm Chemical Reagent Co.,Ltd (China). Lead (II) Iodide (99.99%, trace metals basis) and Lead (II) Bromine (purity, 99.99%) (for Perovskite precursor) was purchased from TCI (Japan), CH_3NH_3Br (MABr) and $CH_3CH_2NH_3I$

(FAI) from Dyesol (Australia). DMF, DMSO, 1,2-dichlorobenzene, 4-tert-butylpyridine (tBP) and lithium bis(trifluoromethylsulfonyl)amine (Li-TFSI) were obtained from Aldrich (U.S.). Tris(2-(1Hpyrazol-1-yl)-4-tert-butylpyridine)cobalt(III) tris(bis(trifluoromethylsul-fonyl)-imide) (FK209-cobalt(III)-TFSI) and spiro-MeOTAD was purchased from Xi'an Polymer Light Technology (China). All reagents were used as received.

2. Solar cells preparation: First, a non-compact fullerene (C_{60}) film were deposited on the clean substrates (indium-doped tin oxide or polyethylene terephthalate/ ultrathin gold) by spin-coating a nearly saturated solution of 28 mM C_{60} dissolved in 1,2-dichlorobenzene with a speed of 2000 rpm for 30 s and annealed at 60°C for 5 min. In order to establish an ultrathin layer of TiO_x, an aqueous solution of $TiCl_4$ was diluted to the concentration varying from 1 mM to 9 mM. The ITO/C_{60} substrates were then immersed into these solutions and kept in an oven at 70°C for 30 min in petri dishes. The $TiCl_4$-treated films were washed with deionized water and dried at 70°C in air for 1 hour. To compare the performance between the bilayer- and TiO_2-based devices, the reference TiO_2-based devices were fabricated using TiO_2 ETLs by spray method at 400°C as previous reported.[1] Subsequently, $FA_{0.85}MA_{0.15}PbI_{2.55}Br_{0.45}$ precursor solution was prepared of 1.1 M Pb^{2+} (PbI_2 and $PbBr_2$) in a mixed solvent of DMSO and DMF (v/v=1:4). Both of the molar ratios for $PbI_2/PbBr_2$ and FAI/MABr were fixed at 0.85:0.15. In a second step, the completely dissolved solution was spin coated onto ETLs in the nitrogen glovebox with the following procedure: first 1000 rpm for 10 s and second 5000 rpm for 30 s with ramps of 1000 and 2500 $rpm\cdot s^{-1}$, respectively. 110 μL of chlorobenzene was rapidly dripped on the rotating substrates during the second spin-coating step 15 s before the end of the procedure. The transparent perovskite film was then heated at 100 °C for 1.5 hours. A spiro-OMeTAD/ chlorobenzene solution (60 mM) with additives of 28 μL 4-tert-butylpyridine (TBP) and 17.5 μL Li-TFSI/acetonitrile (1.8 M) and 8μL FK209-cobalt(III)-TFSI/acetonitrile (0.2 M) was spin coated on top of the active layer at 4500 rpm for 20 s. Finally, 80-nm-thick Au was deposited by thermal evaporation under high vacuum.

3. Characterizations: The *J-V* characteristics of the devices were measured with a Keithley 2400 sourcemeter equipped with a sunlight simulator (XES-300T1, SAN-EI Electric, AM 1.5), which was calibrated using a standard silicon reference cell. The J-V curves of all devices were measured by masking the active area with a metal mask of 1 cm^2. Incident photon to current efficiency (IPCE) was measured as a function of wavelength from 300 to 900 nm (Enli Technology) with dual Xenon/quartz halogen light source. The absorption spectra were recorded using UV/Vis spectrometer (Shimadzu, UV-3600) in the 300 nm - 900 nm range. Confocal PL mapping was carried out with a laser confocal Raman spectrometer (Princeton Instruments, Acton Standard Series SP-2558) and a 485 nm laser (PicoQuant LDH-P-C-485, 0.4 mW with a 1% optical density filter), using a home-built confocal microscope on a 5 × 5 μm^2 sample area.

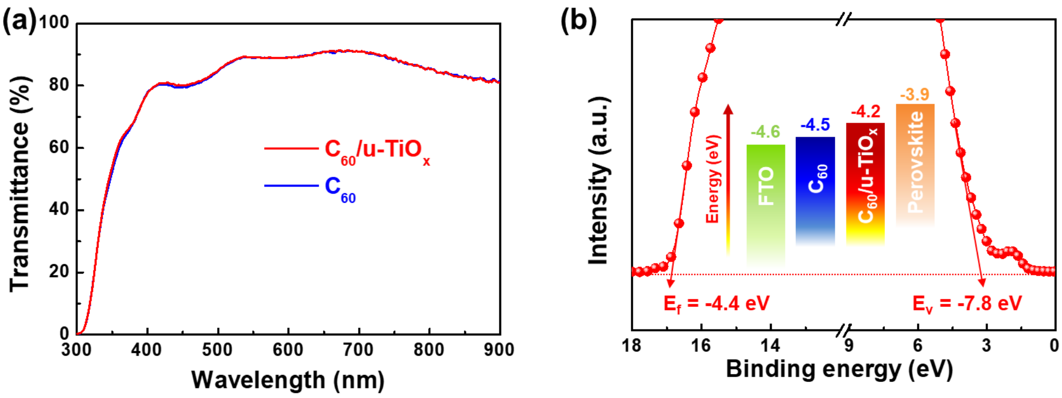

Figure S1. (a) Optical transmission spectra of FTO/C_{60} and FTO/C_{60}/u-TiO_x bilayer samples; (b) UPS measurements of C_{60}/u-TiO_x bilayer and schematics of band alignment for devices based on different ETLs.

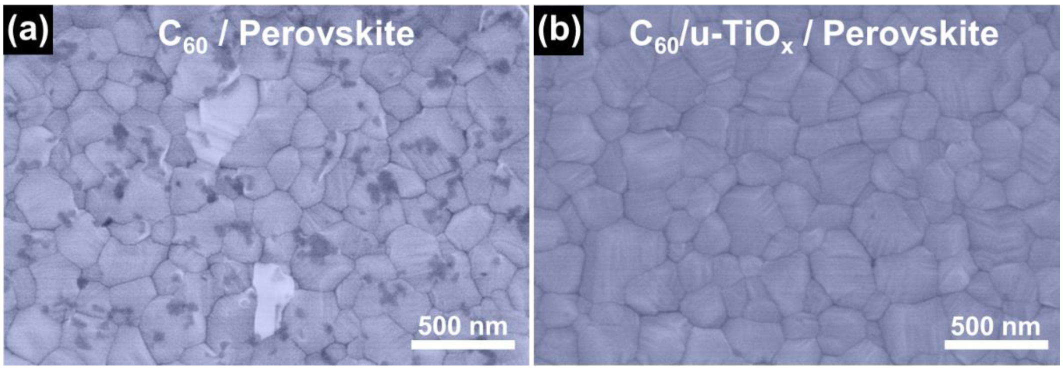

Figure S2. The surface SEM images of partial perovskite films on (a) C_{60} layer and (b) C_{60}/u-TiO_x bilayer.

Table S1. The fitting date from the TRPL spectra of C_{60}/perovskite and C_{60}/u-TiO_x/perovskite samples.

Type	τ_1	τ_2	A_1	A_2	τ_{ave}
C_{60}	15.09	78.29	49.34%	50.66%	68.30
C_{60}/u-TiO_x	9.42	72.18	55.68%	44.32%	63.34

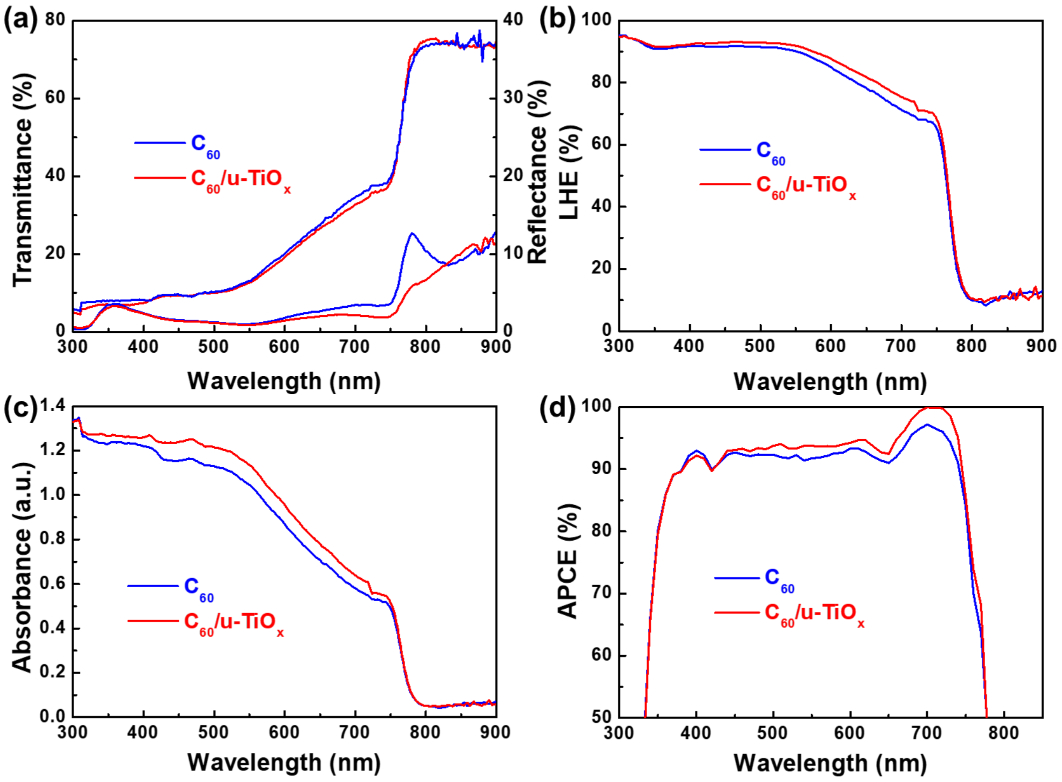

Figure S3. (a) Transmittance and reflectance, (b) light harvesting efficiency (LHE) and (c) absorbance of the ETLs/perovskite/*spiro*-OMeTAD film; (d) absorbed photon-to-current conversion efficiency (APCE) spectra of C_{60} and C_{60}/u-TiO_x bilayer-based PSCs.

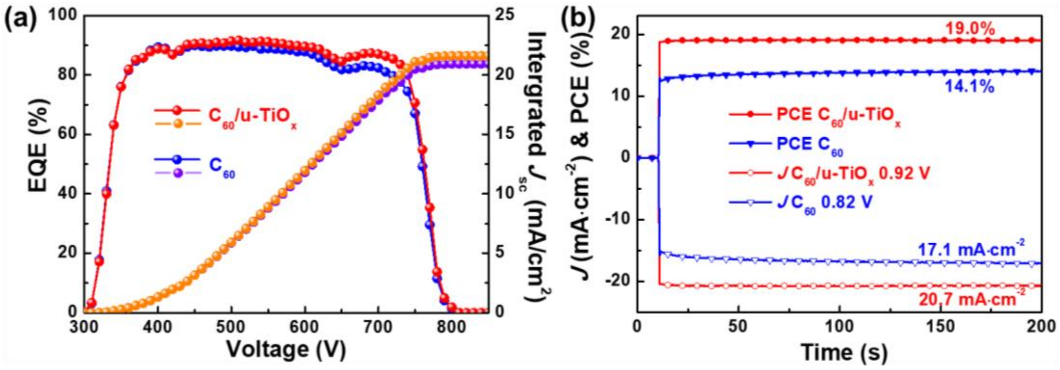

Figure S4. (a) EQE spectra of PSCs with C_{60} and C_{60}/u-TiO_x bilayer ETLs. (b) Steady-state measurement of photocurrent (J_{sc}) and PCE of PSCs with C_{60} and C_{60}/u-TiO_x bilayer.

Table S2. Photovoltaic parameters of PSCs fabricated with C_{60}/u-TiO_x bilayer ETLs with a $TiCl_4$ treatment process varying in solution concentration from 0 to 50 mM measured under AM1.5 illumination.

	J_{sc} (mA·cm^{-2})	V_{oc} (V)	FF (%)	PCE (%)
0 mM	22.51	1.01	62.69	14.27
1 mM	22.07	1.02	70.37	15.78
3 mM	22.38	1.06	75.82	18.01
5 mM	22.65	1.09	77.55	19.21
7 mM	22.72	1.09	77.16	19.05
9 mM	22.39	1.08	76.89	18.63

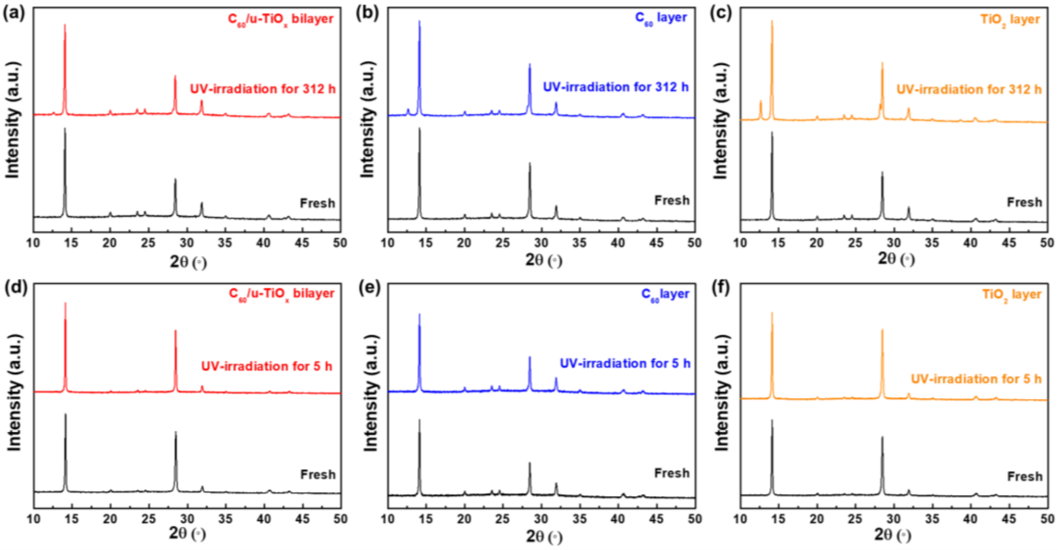

Figure S5. XRD patterns of perovskite films on different ETLs under constant 10 mW·cm^{-2} UV irradiation (λ = 340 nm) in air (≈45% humidity) for (a-c) 312 h and (d-f) 5 h.

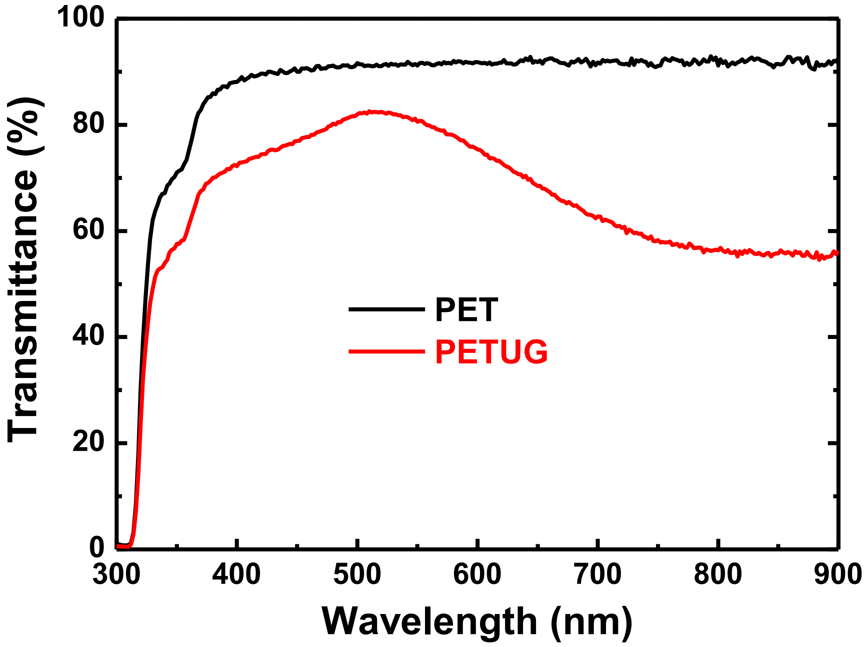

Figure S6. The transmittance of the polyethylene terephthalate (PET) and PET/ ultrathin (8 nm) gold (PETUG) substrates.

Reference:

[1] Y.-K. Ren, X.-H. Ding, Y.-H. Wu, J. Zhu, T. Hayat, A. Alsaedi, Y.-F. Xu, Z.-Q. Li, S.-F. Yang, S.-Y. Dai, *Journal of Materials Chemistry A*, 2017, **5**, 20327-20333.